

# HALOGENS IN THE TROPOSPHERE

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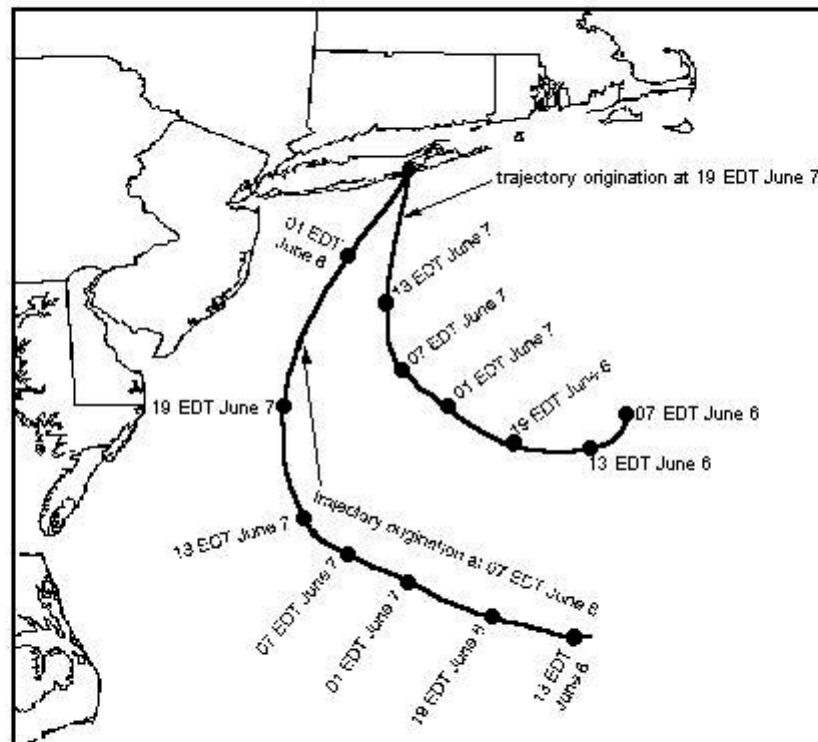
## ***DEPARTMENT OF ENERGY***

Atmospheric Science Program Meeting

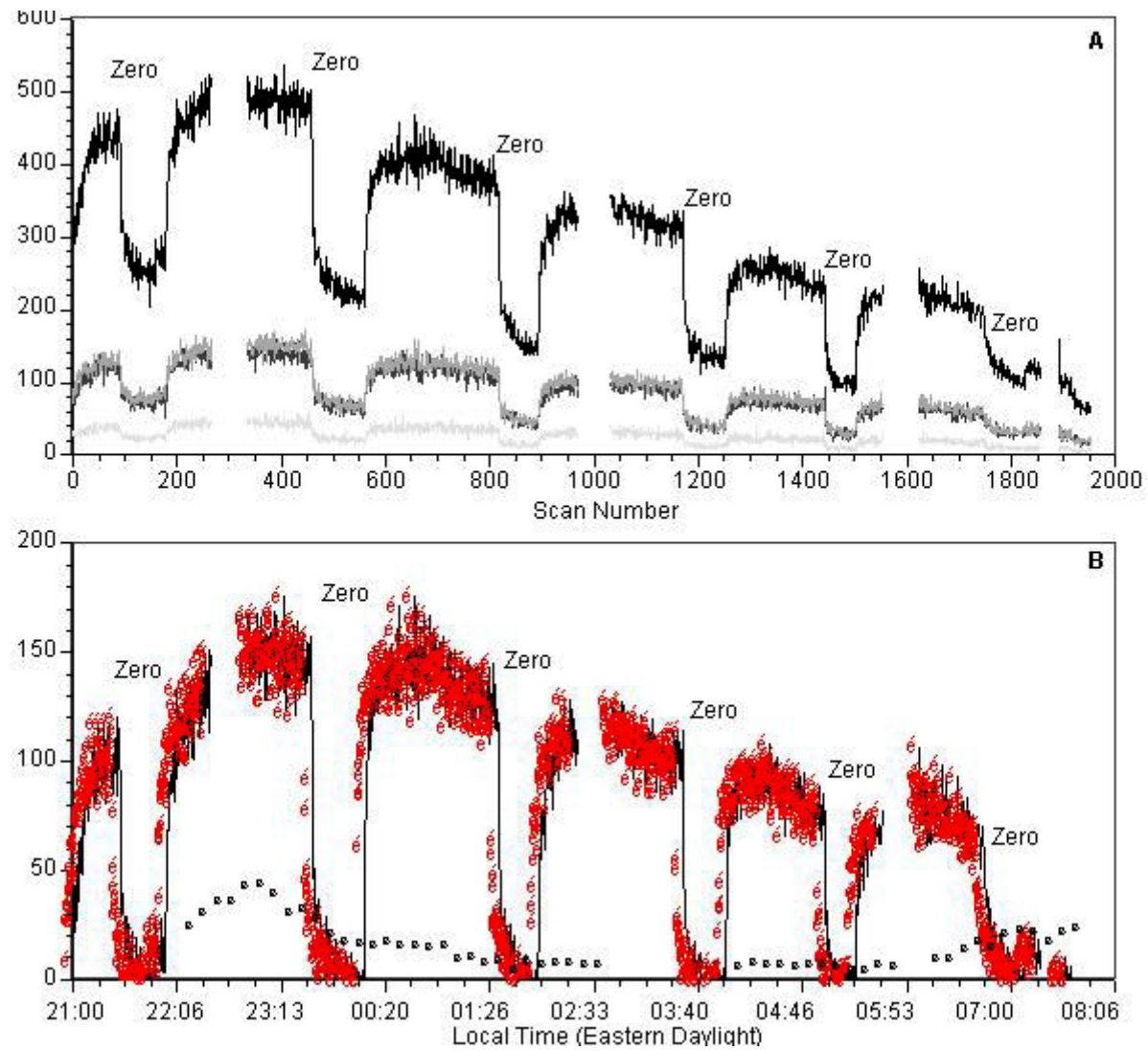
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## SOME EVIDENCE FOR HALOGENS IN THE TROPOSPHERE

- First specific detection and measurement of  $\text{Cl}_2$  off Long Island
- Identification of products of 1-butadiene reaction in air
- First specific detection and measurement of  $\text{Br}_2$  and  $\text{BrCl}$ , at Alert, Canada around polar sunrise



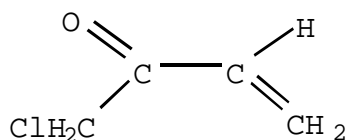
Spicer et al., *Nature*, 394 353 (1998)



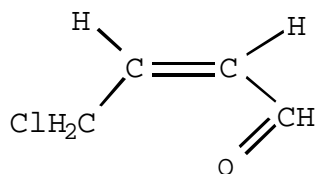
Spicer et al., *Nature*, 394 353 (1998)

## Goals

- Elucidate the mechanism of the reaction of Cl atoms with 1,3-butadiene with or without NO
- Unique chlorine-containing products--markers for Cl chemistry in coastal areas, e.g., as follows:

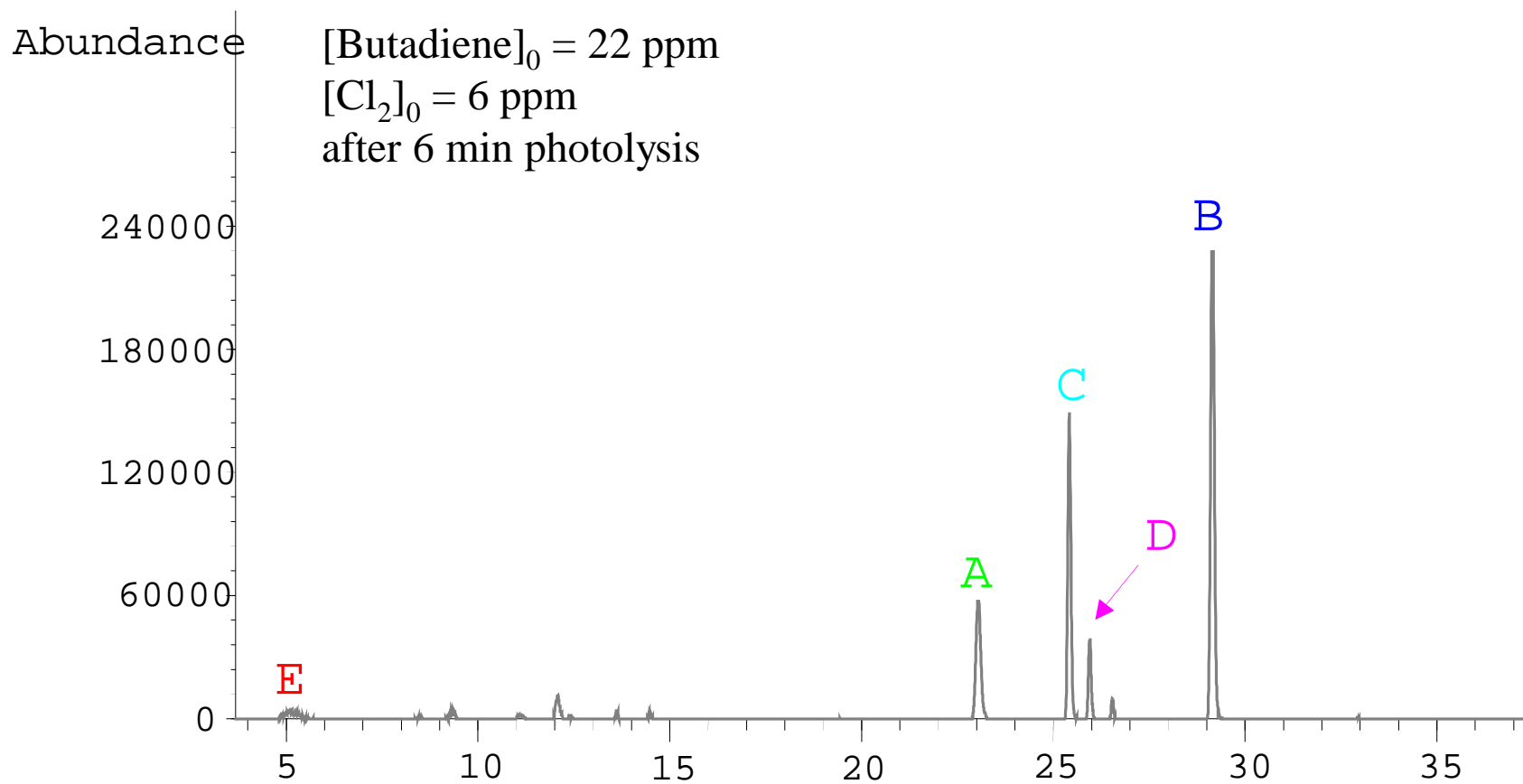


chloromethyl vinyl ketone (CMVK)

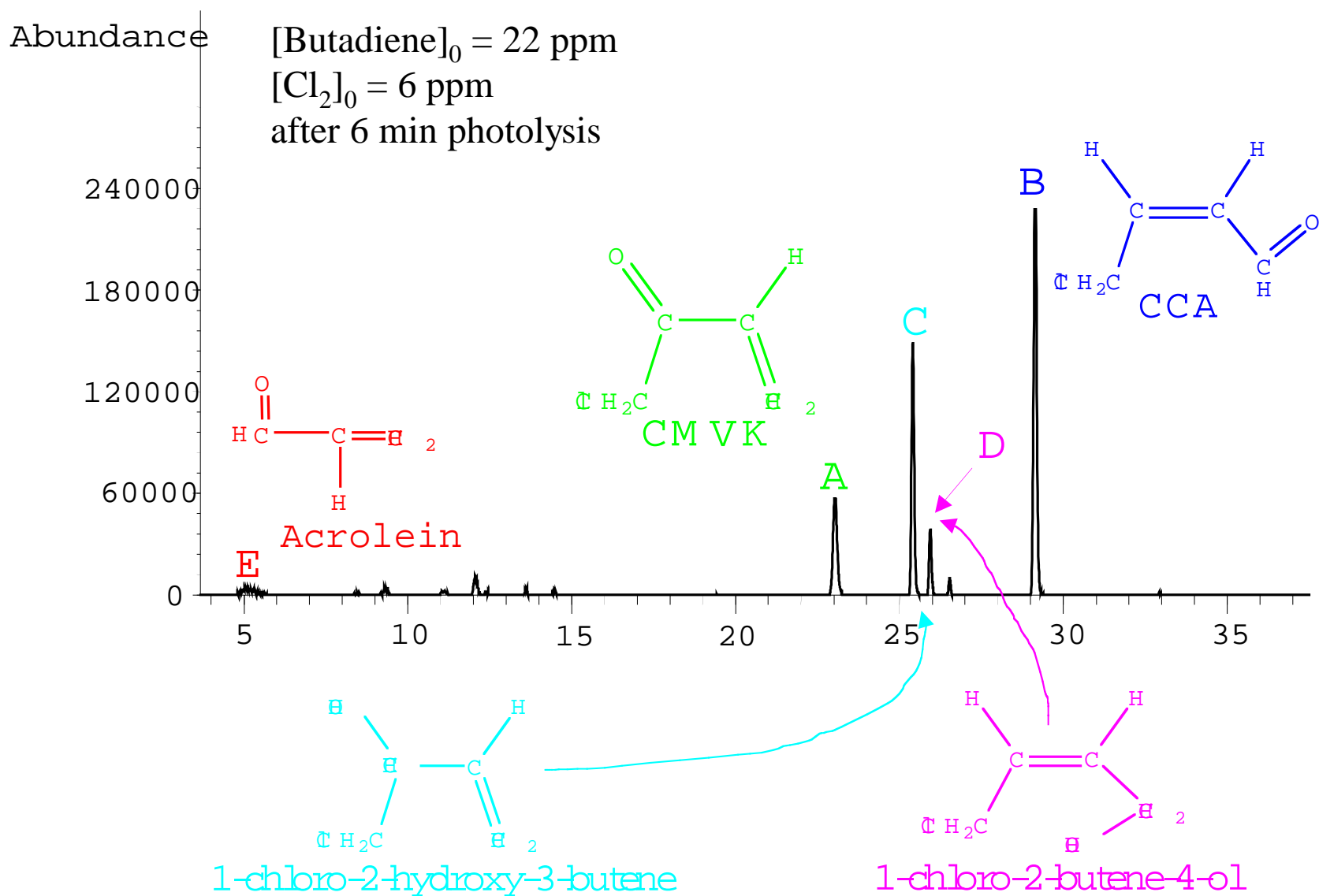


4-chlorocrotonaldehyde (CCA)

# Gas Chromatogram of Products of 1,3-Butadiene + Cl



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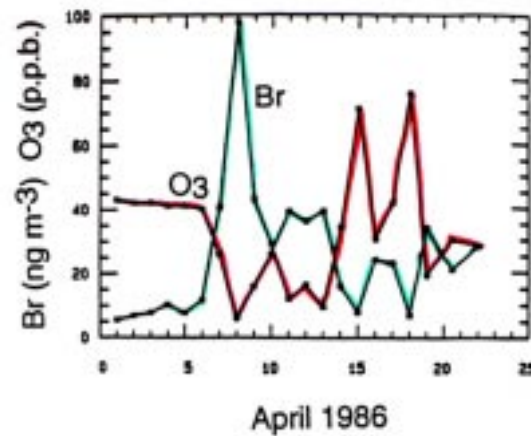






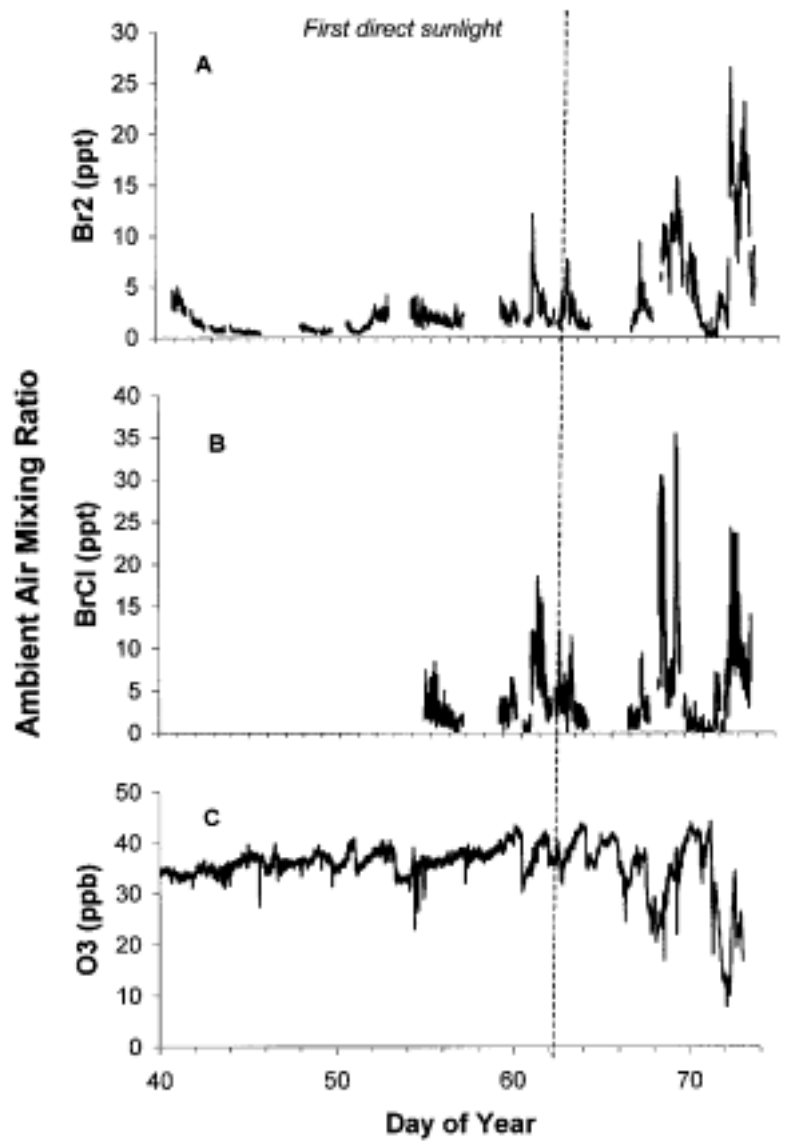
## Bromine → Surface-level Ozone Depletion

- O<sub>3</sub> depletion events in the Arctic spring at surface-level have a strong anticorrelation to gaseous bromine species:

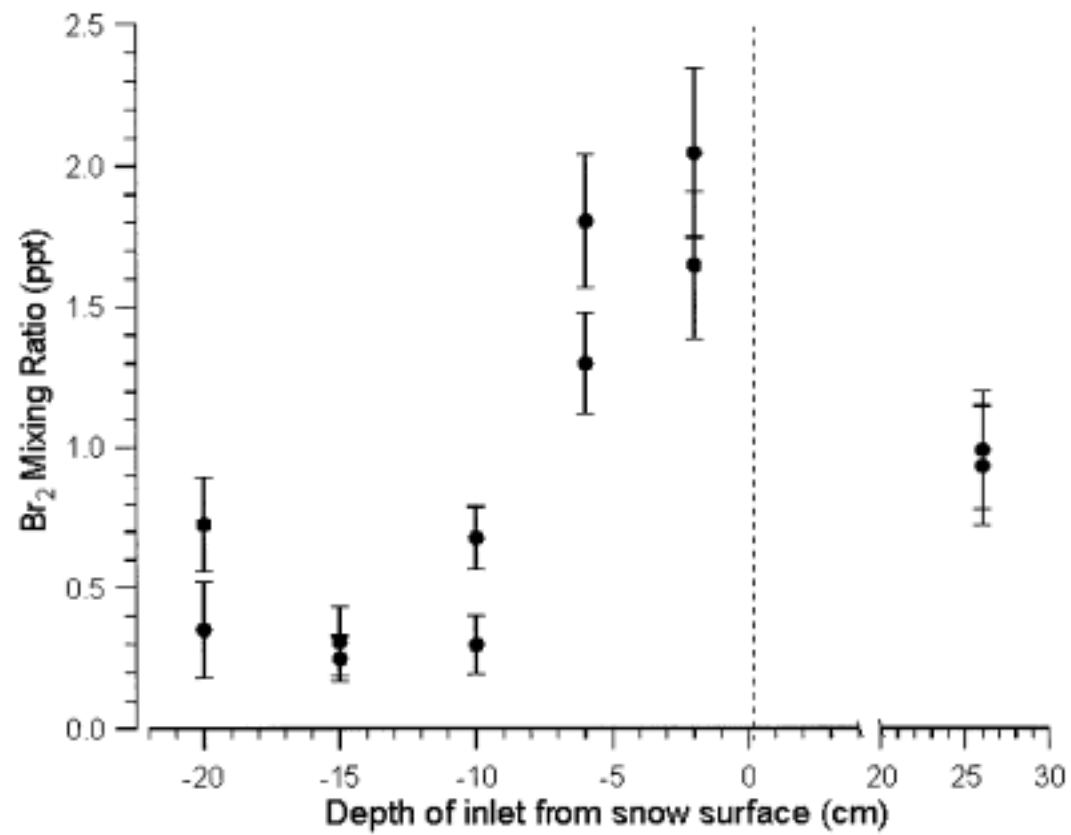


[Barrie *et al.*, 1988]

- An unidentified very large or recyclable dark bromine source is necessary to account for observed bromine concentrations [Fan and Jacob, 1992; Impey *et al.*, 1997].



Foster et al., *Science*,  
291, 471 (2001)



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## BROMINE IN MID-LATITUDES

- Gebestrait *et al.* (1999) reported BrO downwind of salt pans in the Dead Sea, associated lower ozone;
- Dickerson *et al.* (1999) reported large diurnal variations in the MBL over the Indian Ocean that could not be by "conventional" VOC-NO<sub>x</sub>-HO<sub>x</sub> chemistry but were reasonably well matched when bromine chemistry was included; and
- Nago *et al.* (1999) reported ozone destruction just after sunrise at Ogasawara Hahajima Island (NW Pacific Ocean), which was correlated to sea salt particle volume.

## SUMMARY

- Established  $\text{Cl}_2$  is present and may play a role in chemistry of coastal areas;
- Identified unique chlorine-containing products of  $\text{Cl} +$  butadiene reaction (and isoprene) which can be used as "markers" of chlorine atom chemistry in coastal environments; and
- Identified and measured  $\text{Br}_2$  and  $\text{BrCl}$  in Arctic troposphere at polar sunrise.

LABORATORY STUDIES  
OF THE ROLE OF SEA  
SALT BROMINE IN  
DETERMINING  
TROPOSPHERIC OZONE:  
Future Work

- Aerosol chamber studies of NaBr particle reactions;
- Knudsen cell studies of reactions of NaBr;
- Diffuse reflectance Fourier transform infrared studies of NaBr;

- Kinetics and mechanics of Br atom reactions with organics;
- Continue collaborations with Dr. Pavel Jungwirth (Academy of Sciences in Czech Republic) and Professors Benny Gerber and Doug Tobias (UCI) to use molecular dynamics simulations to understand bromine chemistry at the air-water interface; and
- With Professor Donald Dabdub, incorporate chemistry into airshed model.

## ACKNOWLEDGEMENTS

- Department of Energy Atmospheric Science Program
- NATO for support for collaborators carrying out molecular dynamics research
- Meteorological Service of Canada for partial support during Alert study